248-nm Laser Photolysis of $CHBr_3$/O-atom Mixtures: Kinetic Evidence for UV CO(A)-Chemiluminescence in the Reaction of Methylidyne Radicals With Atomic Oxygen

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AFRL's Motivation

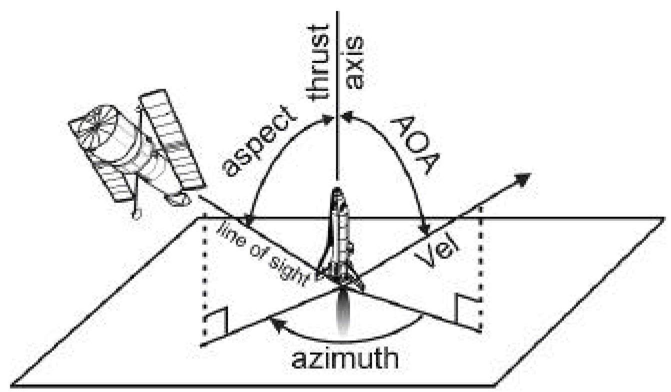
- **Spacecraft Atmospheric Interactions**
- **Chemiluminescent Combustion Processes**

- **Strong Emissions From:**
  - **O(^{1}D), O(^{1}S)**
  - **NH(A)**
  - **OH(A)**
  - **CO(a)**

- **Cause of Chemiluminescence:**
  - **Plume-Atmospheric Interactions**

- **Source Chemistry:**
  - **Precursors? & Formation?**
  - **O-atom Reactions**
  - **Other Reactions**

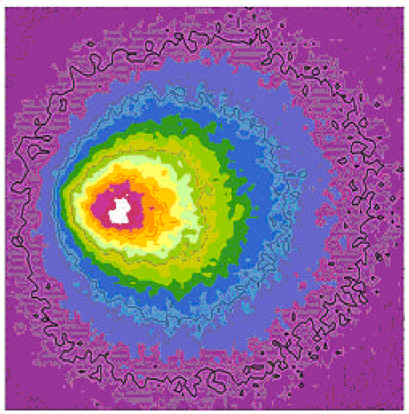
- **Space Experiment**



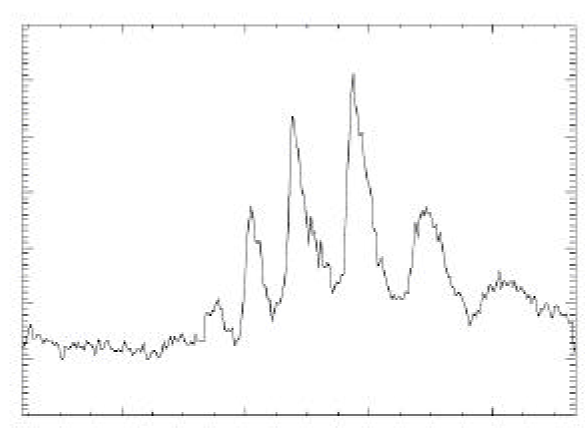
Observation Platforms	**Thrusters**
Space Shuttle	Space Shuttle
Mir Space Station	Progress-M
MSX	Soyuz-TM

UV/Vis Plumes

Radiance Data



Spectral Data



Û Plume Data Û

⇕

Modeling Studies

⇕

Laboratory Studies

⇕

Chemiluminescent Processes

⇕

Identify Spacecraft Atmospheric Interactions

Proposed CO(a) Source Chemistry

- Unreacted Fuel ® ® Precursor(s)
- Precursor(s) + O ® Products

  ® CO($a_{(v')}$) + R

  ® CH_2 + OR'

  ® CH + OR''

- k = 1.3 x 10^{-10}

  CH_2 + O ® Products

  ® CO($a_{(v'£8)}$, $a'_{(v'£5)}$, $d_{(v'£1)}$) + H_2

  CO + H_2 (Main)
  2H + CO (~ 20%)
  H + HCO (HCO*)
  CH + OH (~ 6%)

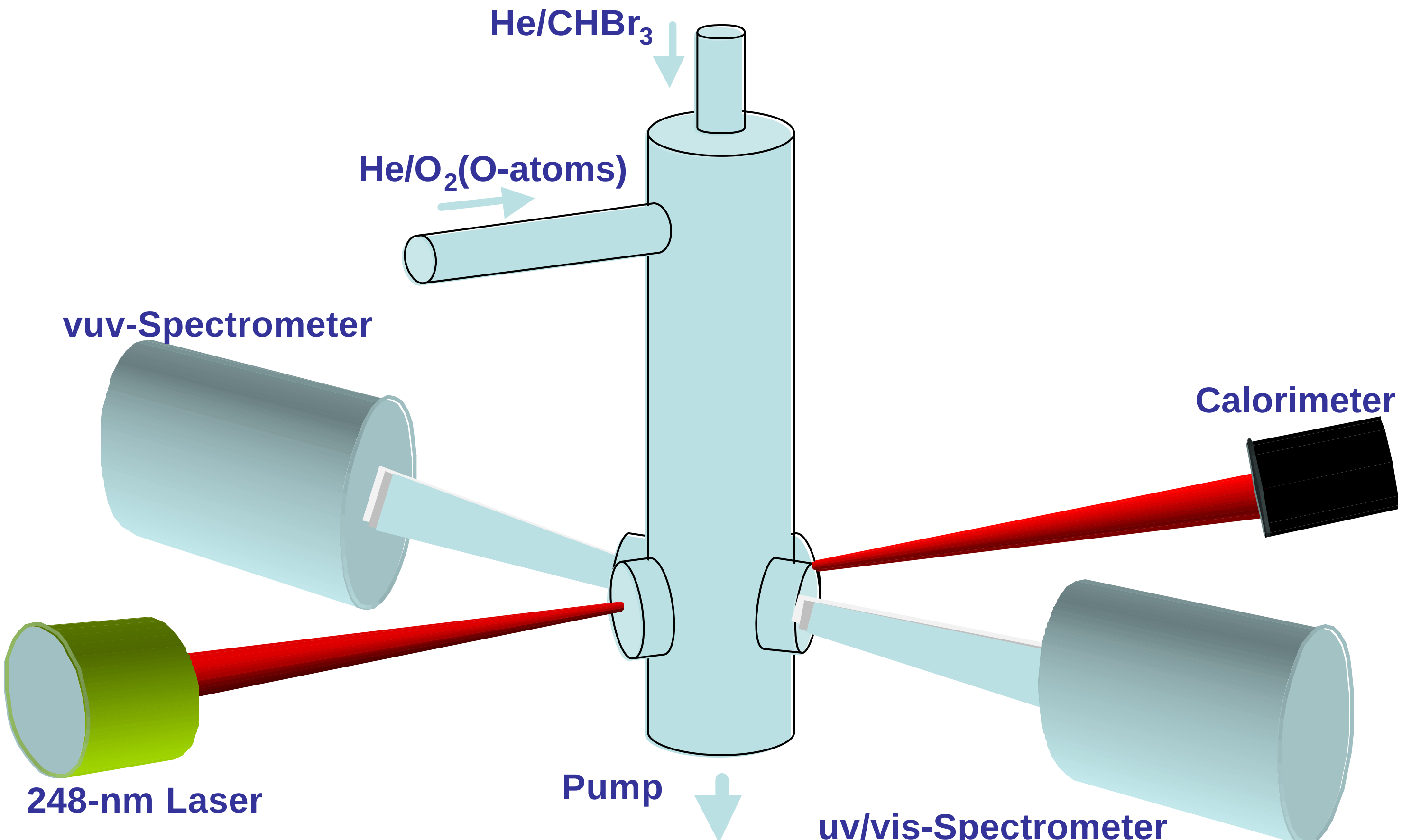
- k = 9.5 x 10^{-11}

  CH + O ® Products

  ® CO($a_{(v'£8)}$, $a'_{(v'£5)}$, $d_{(v'=0)}$) + H

  CO + H (Main)
  HCO (HCO*)
  HCO^+ + e^- (~ 0.03%)
  C + OH (? +ve E_a)

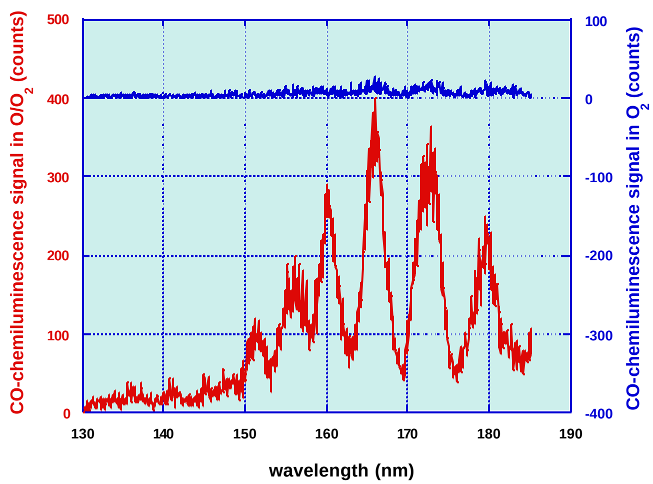
Apparatus



He/CHBr3
He/O2(O-atoms)
vuv-Spectrometer
Calorimeter
248-nm Laser
Pump
uv/vis-Spectrometer

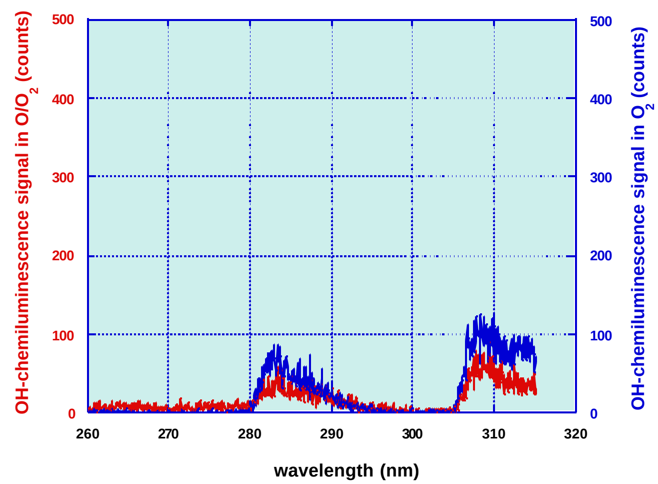
Comparison of CO & OH-Chemiluminescence

Strong CO(A) Signal in O/O_2



Very Weak CO(A) Signal in O_2 only

Weakened OH(A) Signal in O/O_2



Strong OH(A) Signal in O_2 only

$k = (2.3\text{-}5.9) \times 10^{-11}$

- **CH + O_2 ® Products**
  ® CO($a_{(v'£4)}$, $a'_{(v'=0)}$) + OH

CO + OH (~ 20%)
CO_2 + H (~ 30%)
HCO + O (~ 20%)
H + CO + O (~ 30%)
CO + OH(A) (~ 0.48%)

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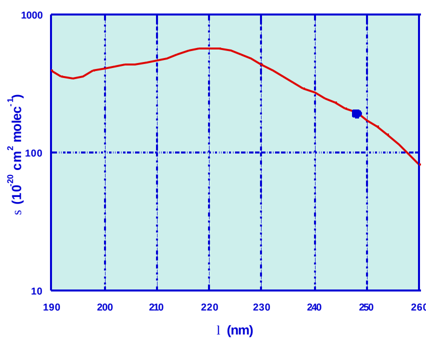
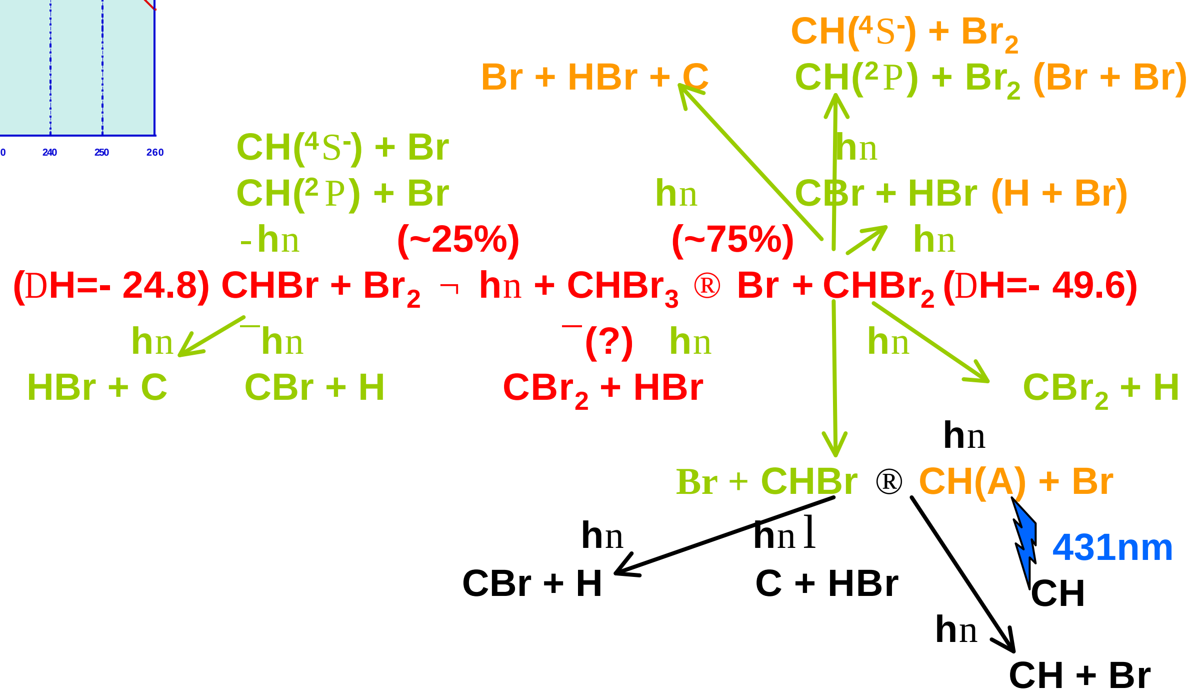
Bromoform Photolysis





CO(A) Source Reactions

- **Chemiluminescence Intensity Varied as (Laser Fluence)^2**

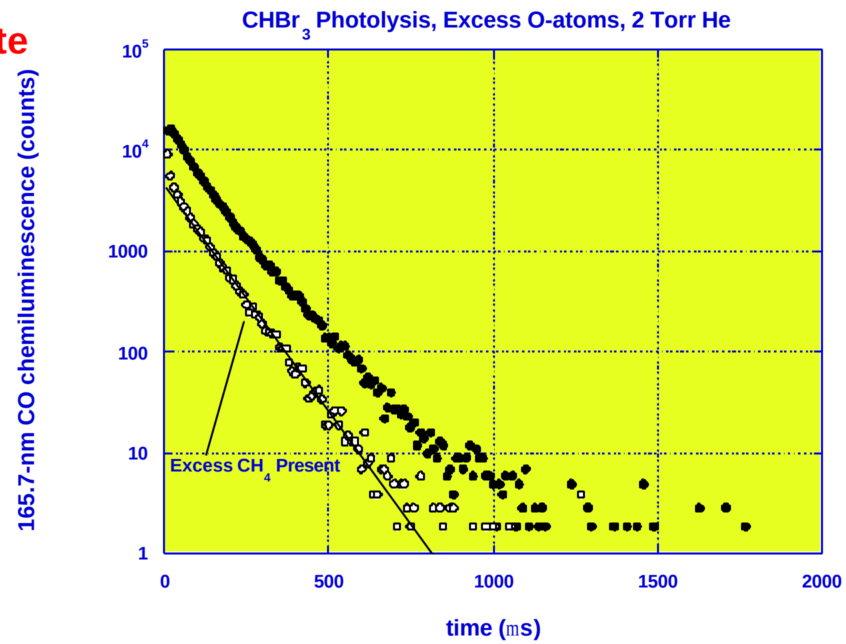
	DH$^o_{298K}$(kcal mol^{-1})
C(^{3}P) + O(^{3}P) ® CO(A^{1}P)	(-71.8)
CHBr + O(^{3}P) ® HBr(X^{1}S$^+$) + CO(A^{1}P)	(+1.3)
CH + O(^{3}P) ® H(^{2}S) + CO(A^{1}P)	(+9.2)
CBr + O(^{3}P) ® Br(^{2}P$_{3/2}$) + CO(A^{1}P)	(+3.8)
CBr$_2$ + O(^{3}P) ® Br$_2$(^{1}S^+_g) + CO(A^{1}P)	(+29.1)

- **Diatomics or Triatomics Need to be Internally Excited**

Time Resolved CO(A)-Chemiluminescence

❑ **Bimolecular Reaction Rate Coefficients of Added Substrate When CH_4 Present**

$k_{O_2} = (2.2 \pm 0.3) \times 10^{-11}$
$k_{N_2O} < 7 \times 10^{-14}$
$k_{NO} = (3.4 \pm 0.5) \times 10^{-11}$
$k_{H_2} < 2 \times 10^{-13}$
$k_{CH_4} < 6 \times 10^{-14}$



❑ **(C + O) Not the Source**

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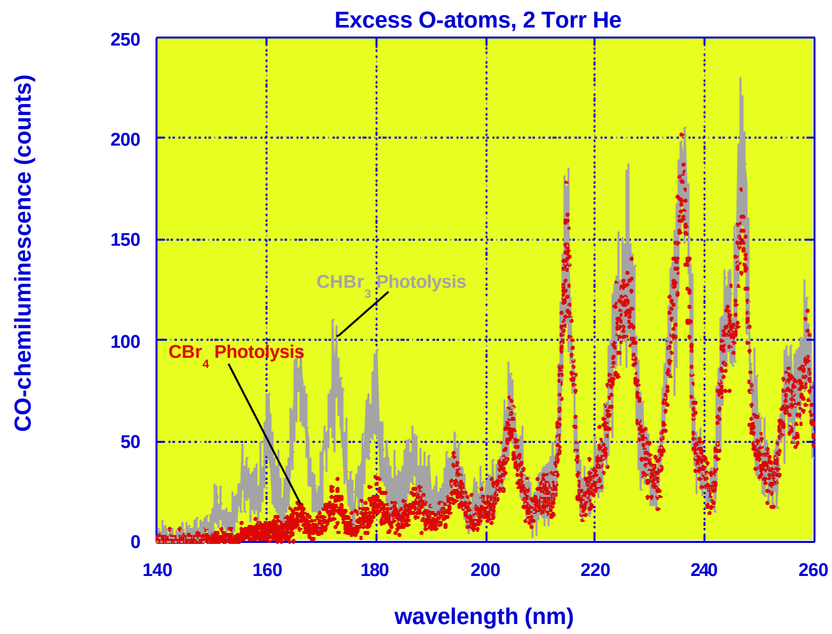
$CHBr_3$ Versus CBr_4 Photolysis



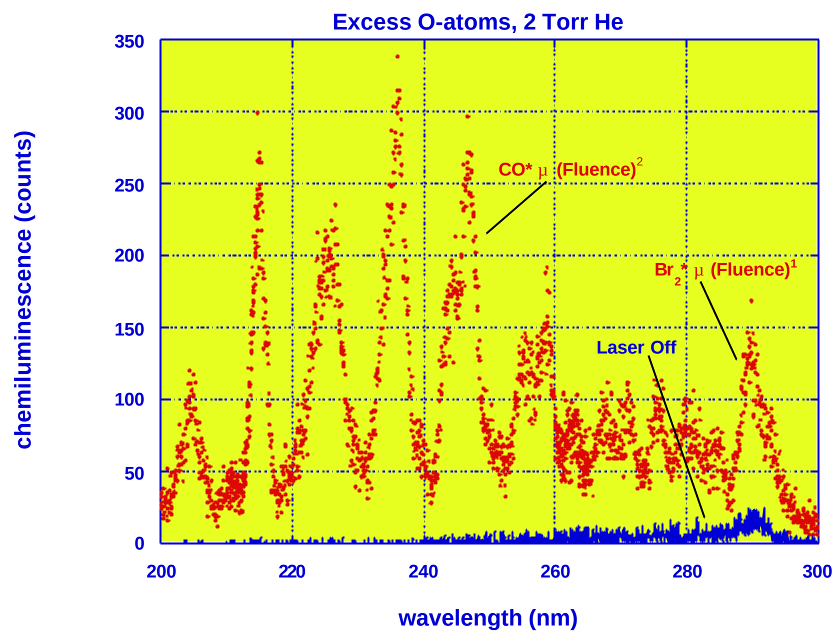
- **Stronger VUV Signal in $CHBr_3$ Photolysis**

  – **($CH^{\#}$ (or $CHBr^{\#}$) + O) Important**

- **Signal in CBr_4 Photolysis Varies as $(\text{Fluence})^2$**

  – **($CBr_2^{\#}$ + O) not Important, Since Br_2^* Signal Varies as $(\text{Fluence})^1$**

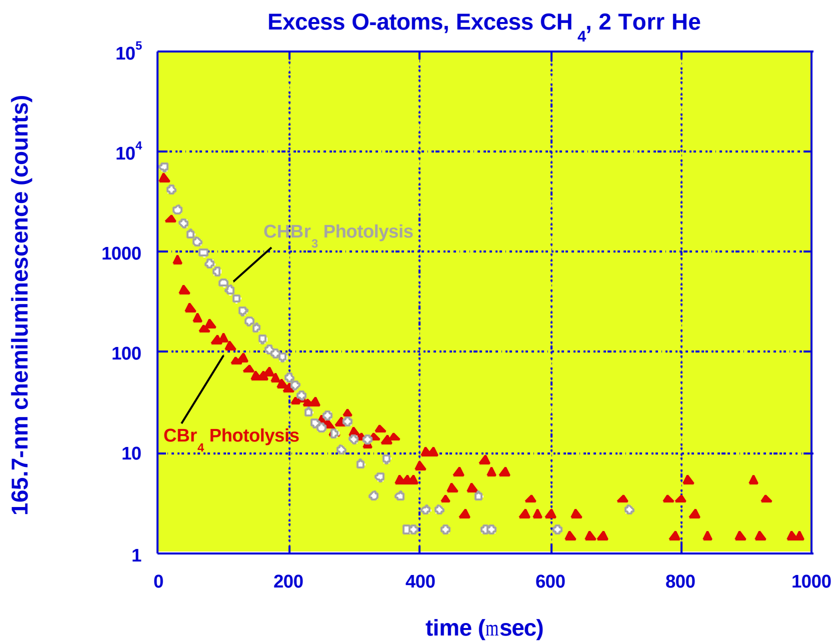
CBr_4 Photolysis



- ❑ CBr_2 + O ® CO + Br_2*
- ❑ CBr_2 Formed in Absence of Photolysis
- ❑ CBr_2 Formed in Photolysis
- ❑ CBr + O ® CO* + Br

CBr_2 + O ® CO* + Br_2 not Important

$CHBr_3$ Versus CBr_4 Photolysis



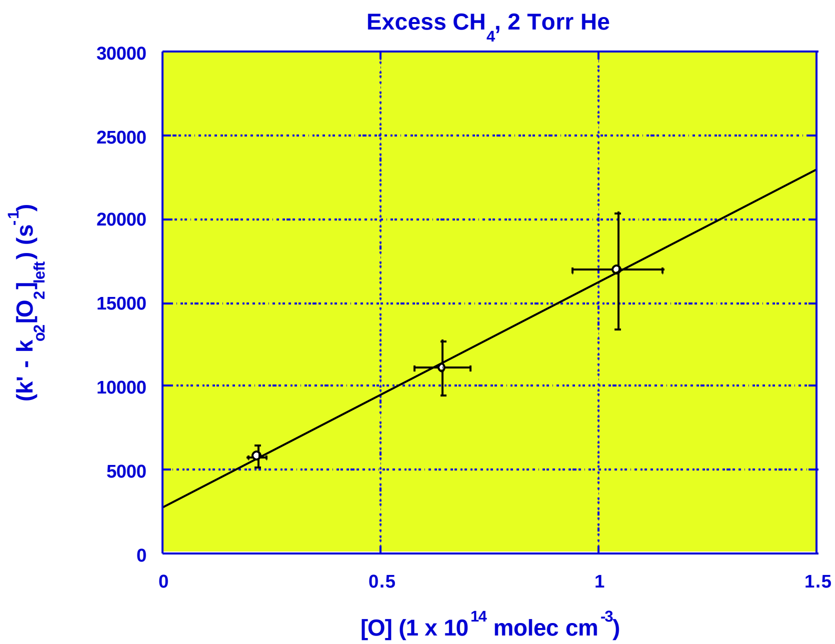
- $CHBr_3$
  $k_{O_2} = (2.2 \pm 0.3) \times 10^{-11}$
- CBr_4
  $k_{O_2} = (2.4 \pm 0.4) \times 10^{-12}$

($CBr^{\#}$ + O) Source is not as Important as ($CH^{\#}$ + O) in $CHBr_3$ Photolysis

- $CHBr^{\#}$ has Very Short Lifetime (~ 5 μs) and $k_{(CHBr + O_2)} < 2 \times 10^{-14}$

($CHBr^{\#}$ + O) Source not Important in $CHBr_3$ Photolysis

CH(a$^4\Sigma^-$) + O Reaction Rate Coefficient

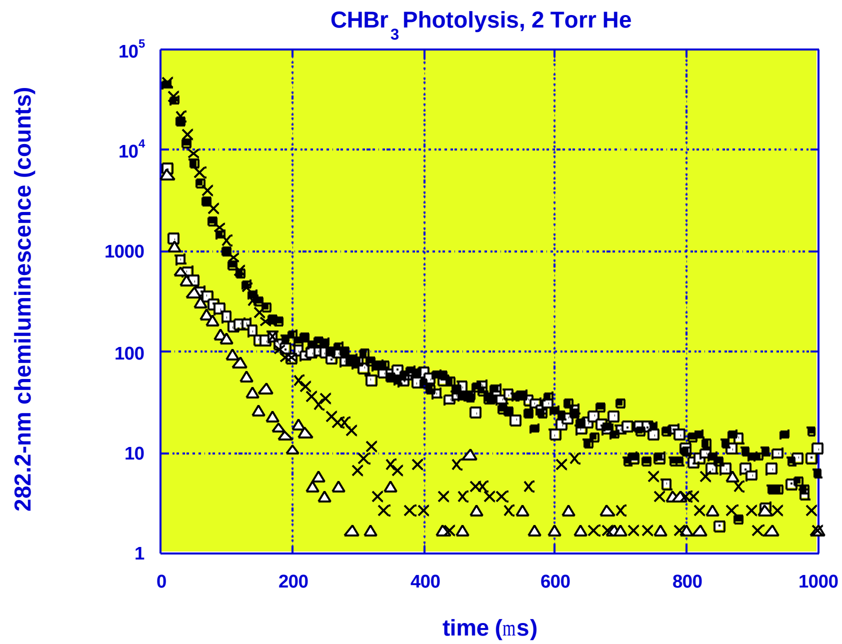


- $k_{(CH(a) + O)}$ = (1.35 ± 0.47) x 10^{-10}

Previously:

- $k_{(CH(X) + O)}$ = (9.5 ± 1.4) x 10^{-11}

282.2-nm Signal



❑ **Absence of O-atoms**

X-trace: (O_2, 8.8 x 10^{14})
D-trace: (O_2) + (CH_4, 5.0 x 10^{15})

–

CH(X^2P) + O_2 ® CO + OH(A)

CH(a^4S$^-$) + O_2 ® CO + OH(A)

❑ **5.0 x 10^{13} of O-atoms**

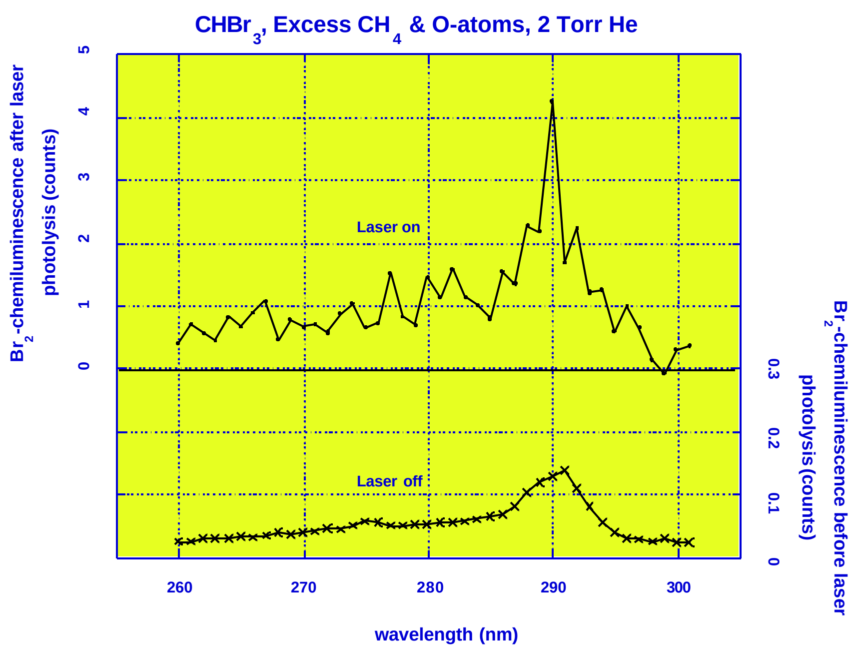
• -trace: (O_2, 8.8 x 10^{14})
? -trace: (O_2) + (CH_4, 5.0 x 10^{15})

–

CBr_2 + O ® CO + Br_2(D)

(CBr_2 + CH_4) Slow Reaction

Br_2*-Chemiluminescence



- **Laser off**

$CHBr_3$ + O ? CBr_3 + OH
CBr_3 + O • CBr_2 + BrO

–

CBr_2 + O • Br_2^* + CO

- **Laser on**

Br_2^* µ (Fluence)[1]

–

$CHBr_3$ + hn ® $CHBr_2$* + Br
2
$CHBr_3$ + hn ® CBr_2 + HBr
$CHBr_2$* + hn ® CBr_2 + H
$CHBr_2$* + O ® Br_2^* + HCO
$CHBr_2$ + O ® CBr_2 + OH
$CHBr_2$* + O ® CBr_2 + OH(A)
CHBr* + O ® CBr + OH(A)

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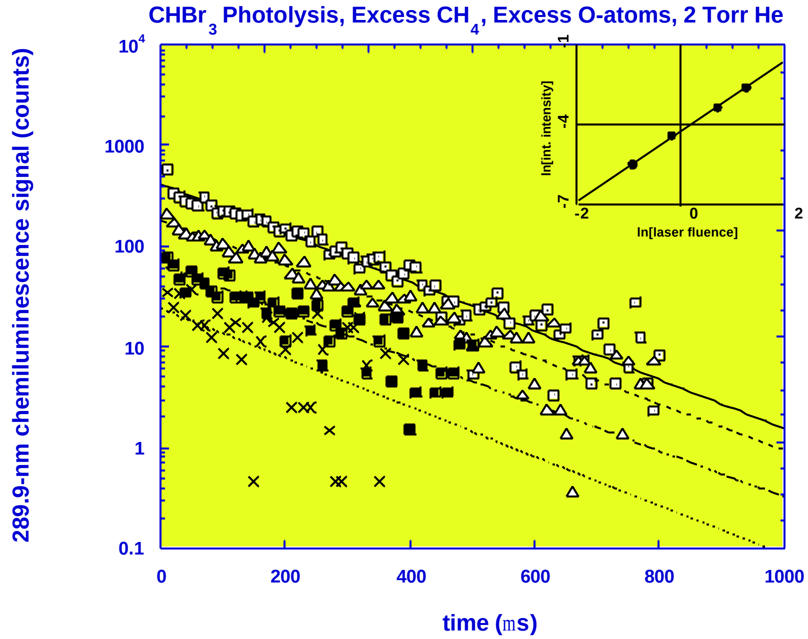
Time Resolved Br_2*-Signal



- **Fast Br_2^* Rise**
- **Also:**

k_{O_2} < 9 x 10^{-14}
k_{CH_4} < 7 x 10^{-14}
k_O = (5.4 ± 1.0) x 10^{-11}

$CHBr_3$ + hn ® CBr_2 + HBr

Less Important
CBr_3 + hn ® CBr_2 + Br

- **Since:**

CBr_4 + hn ® CBr_3* + Br
CBr_2 + Br { f?

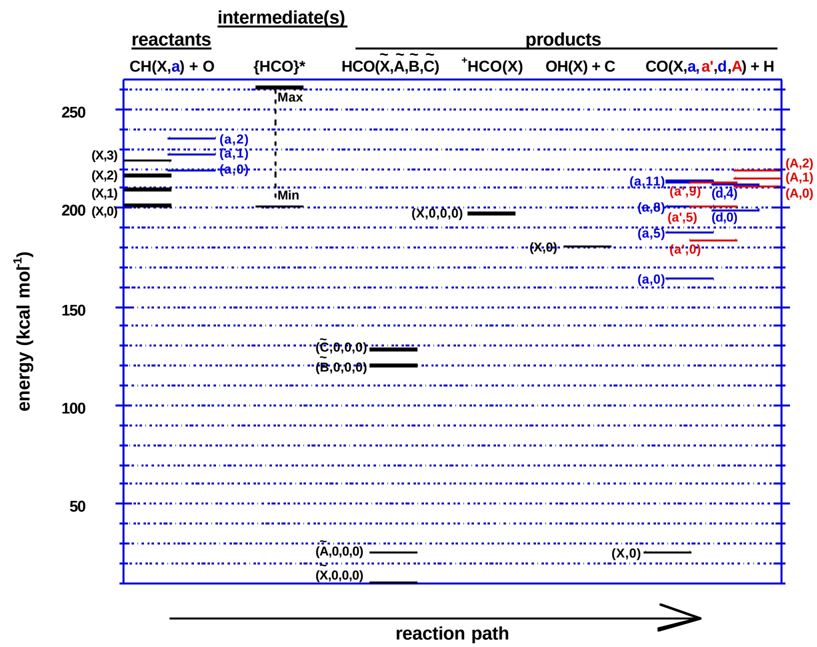
CBr_4 + hn ® CBr_2 + Br_2 { f?

CO* Production Mechanism

CH# + O ® {HCO}* ® CO* + H

M

CO* ® CO(X,a,a',d,A)



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Conclusions

- 248-nm Photolysis of $CHBr_3$/O-atom Mixtures

Strong Emissions From:

  - CO(A), CO(a)
  - OH(A) when O_2 Present
  - NH(A) when NO Present
  - Br_2(D)

Kinetic & Laser Fluence Trend Analyses of the Chemiluminescence:

  - CH + O
  - CH + O_2 (NO)
  - CBr_2 + O

- 248-nm Photolysis of CBr_4/O-atom Mixtures
  - CBr + O
  - CBr_2 + O

- Thermospheric O-atoms + Plume Fragments (CH) ® UV Emissions